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EFFECT OF pH ON THE COMPOSITION OF THE CLATHRATES OF TETRACYANOCOMPLEXES Ni[II] BY METHODS OF THERMAL ANALYSIS

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ABSTRACT

The aim of this study was the isolation of the host model compounds of the tetracyano complexes of Ni[II] with the chemical formula $Ni(NH_3)_m$ $Ni(CN)_4$ from solutions at different pH. The study of the chemical composition of the host component and their thermal stability is discussed.

After the isolation of the host component, some water was always found to be present in the material in the solid state. According to its behavior in the solid state the compound of general formula $Ni(NH_3)_mNi(CN)_4 \cdot n\ H_2O$ is of the clathrate type. The amount of water and ammonia ligands depends on the pH, and was determined by TG, DTA, DSC and combined DSC/GC measurements.

INTRODUCTION

One of the most stable complexes of nickel is the anion $[Ni(CN)_4]^{2-}$, but it is rapidly decomposed by acids with formation of hydrated $Ni(CN)_2$ [1]. The slow addition of dilute sulphuric acid to a boiling aqueous solution of $K_2[Ni(CN)_4]$ yields the hydrate of the type $Ni(CN)_2 \cdot 2\ H_2O$ [2], which according to X-ray studies [3,4] is in the form of $NiNi(CN)_4 \cdot n\ H_2O$. Different hydrated forms are known [1-3] with values of n depending on the conditions of the preparation. By simultaneous addition of dilute solutions of Ni^{2+} and KCN to boiling water the $NiNi(CN)_4 \cdot 3\ H_2O$ form was obtained. Hydrates of various compositions with layered structure have been found [2,3] with two types of bonded water. If $n > 2$, two molecules of water are coordinated to Ni^{2+} and the rest in layers and it is possible to differentiate between the two forms by spectroscopy.

This layer structure is closely related to that of $Ni(NH_3)_2Ni(CN)_4 \cdot 0.5\ H_2O$ ($Ni(CN)_2 \cdot NH_3 \cdot 0.25\ H_2O$) determined earlier [5], but this was preceded by work on its compounds with aromatic guest component [6] of general formula $Ni(NH_3)_2Ni(CN)_4 \cdot 2\ G$ (G = aromatics). The layered form

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has also been found in analogous compounds $Ni(NH_3)_2Pt(CN)_4 \cdot n\ H_2O$ [7] and others.

The compounds of the general formula $Ni(NH_3)_2Ni(CN)_4 \cdot n\ H_2O$ have various non-stoichiometric forms [1]. The compounds as the result of the action of anhydrous liquid ammonia, dry ammonia gas or concentrated aqueous ammonia have been described [8,9].

The results of the sorption experiments with non-stoichiometric compounds proved that their water constituent could be replaced by other organic molecules [10,11]. Similar properties were obtained [12] after partial deammination of the model compounds of the type $M(NH_3)_mM'(CN)_4 \cdot n\ H_2O$ with various m values [13], including $m = 0$. Therefore, the preparation of the host model compounds forming the clathrates of tetracyano complexes is interesting for the study of the thermal stability of the clathrates used as sorptive materials.

EXPERIMENTAL

Preparation

The preparation of the host model compounds for the clathrate tetracyano complexes of general formula $Ni(NH_3)_mNi(CN)_4 \cdot n\ H_2O$ is simple. The methods described in the literature [8,9,11,14] were used. By mixing solutions of Ni[II] (6 g $NiCl_2 \cdot 6\ H_2O$ in 25 ml H_2O) and KCN (3 g KCN in 25 ml H_2O), $Ni(CN)_2$ was prepared, which was immediately dissolved by adding 28 ml NH_4OH (25%). The resultant solution was simultaneously cooled and mixed with acetic acid (60%) to lower the pH value and a precipitate of the host compound was obtained. The precipitated compound was filtered and then washed with ethyl alcohol, ether and kept in a dessicator over silica gel.

All starting compounds were of p.a. purity grade. As a source of Ni [II], it is possible to use $NiSO_4 \cdot 7\ H_2O$ instead of $NiCl_2 \cdot 6\ H_2O$. The pH value was measured by Compensator E 388 Methrom Herisau with a combined electrode. The pH value of the solution was lowered step by step from 12 to 8, 7, 6 and 5. At these pH values the prepared compounds were isolated.

Analysis

Elemental analyses were estimated with a Hewlett Packard CHN Model 185. The metal ion Ni[II] was analyzed gravimetrically with dimethylglyoxime. The structure of compounds was checked by the KBr disc technique using an IR spectrometer Perkin–Elmer Model 577.

Thermal decomposition

All TG, DTG and DTA analyses of prepared compounds were measured up to 600°C in air on a Derivatograph MOM OD 102, Paulik–Paulik–Erdey, with equal parameters (weight of sample 200 mg; sensitivities: TG, 200 mg; DTA, 1/5; DTG, 1/5; heating rate, 6° min^{-1}; reference material, Al_2O_3).

DSC measurements and DSC / GC analysis

The calorimetric measurements were performed with a Perkin–Elmer DSC 2 using nitrogen atmosphere, sensitivity 10 mcal s^{-1} and heating rate 5 K min^{-1}. The measured signal was registered with the TZ 4100 recorder (Laboratorni přistroje, ČSSR). The sample of 3–4 mg was placed in an aluminium sample pan with pinhole. An empty pan was used as reference.

The degradation products (H_2O, NH_3) were injected into a SCH 7801 gas chromatograph (Chemoprojekt, Satalice, ČSSR) by means of an injection valve with a sample loop (350 μl). The components of the mixture were separated on a 2 m column packed with Porapak Q at 100°C and detected with a TCD detector.

RESULTS AND DISCUSSION

After the isolation of the host model compound of the clathrate tetracyano complexes Ni[II] from the solution, a definite amount of water was found in the solid state, which specifies the clathrate type of compound. In order to obtain information about the influence of pH on the chemical composition of clathrate compounds and their properties in the solid state, attention was paid to the samples prepared at pH 8 and 5. In these pH regions, the compounds can be easily isolated and obtained with rather good yields and they contain a definite amount of water bonded in clathrate form. The relative amounts of water and ammonia depend on the pH value in the solution.

The CHN analysis of compounds prepared at pH 8, 7, 6 and 5 agreed with the results of thermal analysis and IR spectra measurements and gravimetric estimation of Ni[II].

The IR spectra of the clathrate compound isolated at pH 5 and at pH 8 are shown in Fig. 1(a) and (b), together with the partially degraded samples prepared by heating to 190°C. At this temperature gaseous products (H_2O) were observed according to TG and DTA curves.

The ammonia vibrations are sensitive to the partial decomposition connected with the loss of water. This phenomenon is observable in the spectral bands of partially decomposed lattices [15]: $\delta_a(NH_3)$ 1610 cm^{-1}, $\delta_s(NH_3)$ 1230 cm^{-1}, $\nu_a(NH_3)$ 3390 cm^{-1} and $\nu_s(NH_3)$ 3300 cm^{-1}.

The number of NH_3 ligands m may be equal to 8 [13]. Partial decomposition also occurs (as a result of the interactions between water and the weakened tetracyano complex sheet) in compounds without the maximum content of ammonia ligands. The band at 1610 cm^{-1} can be assigned to

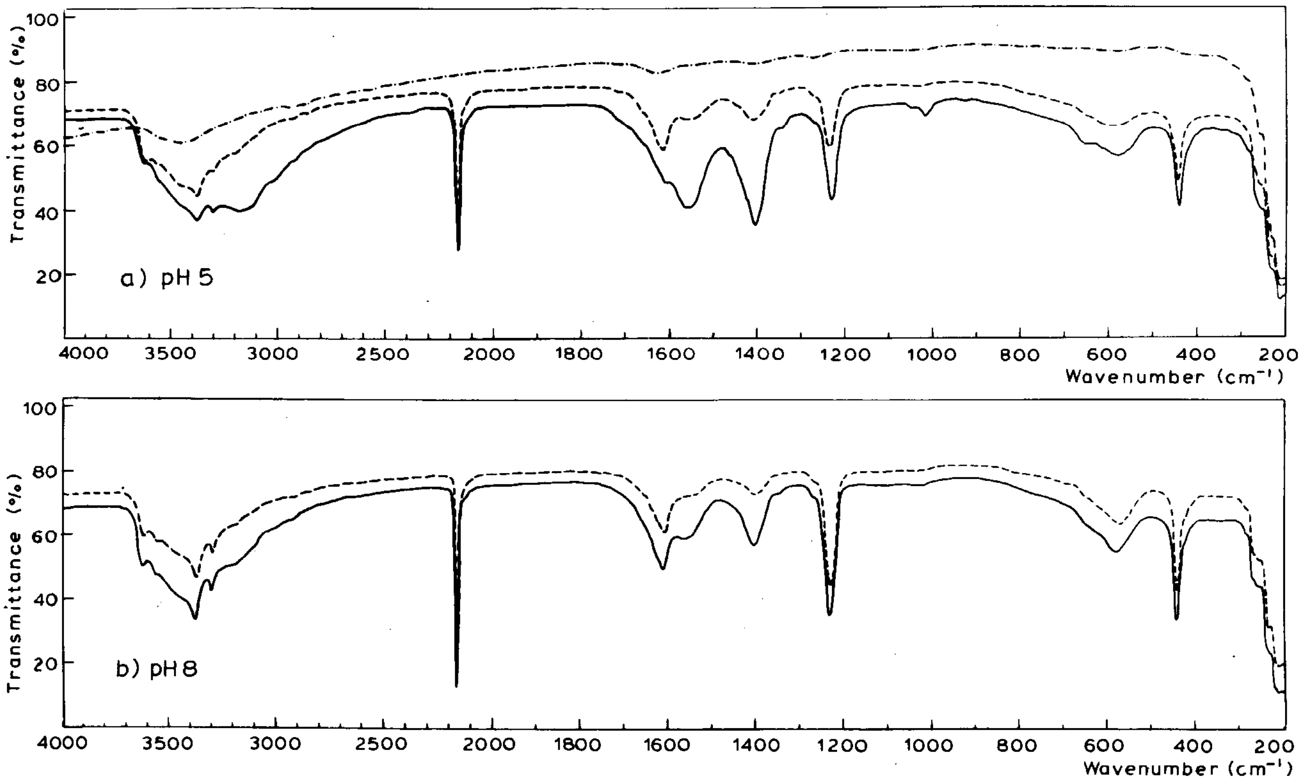

Fig. 1. IR spectra of $Ni(NH_3)_mNi(CN)_4 \cdot n\ H_2O$. (a) pH 5: ———, $m = 2$, $n = 4$; - - - - - -, $m = 2$, $n \rightarrow 0$ (after heating to 190°C); ·—·—·, KBr. (b) pH 8: ———, $m = 2$, $n = 1.9$; - - - - - -, $m = 2$, $n \rightarrow 0$ (after heating up to 190°C).

$\delta_d(H_2O)$ but in this case $\delta_a(NH_3)$ is preferred. The band observed in the region 1550–1560 cm^{-1} can be assigned to $\delta_d(H_2O)$. This is demonstrated by the decrease of the intensity of this broad band if both spectra in Fig. 1(a) and (b) are compared.

On the basis of X-ray diffraction studies [6,16,17], the host lattice of Hofmann-type clathrates is known to consist of layers of two-dimensional tetragonal sheets formed from tetracyanonickelate ions coordinated to bridging diammine metal cations. Similarly, as in the benzene clathrate $Ni(NH_3)_2Ni(CN)_4 \cdot 2\ C_6H_6$, the water is incorporated between these sheets and it is in interaction with ammonia ligands. The frequencies of NH_3 are therefore greatly influenced [15] as in the case of metal–ammonia interactions. The small absorbance was again found in the degraded samples due to the resorption of water during the measurement of IR spectra. This is in agreement with the sorption ability of tetracyano complexes [12].

On the basis of TG and DTA measurements (pH 8, 7, 6, 5) we found that the decomposition of samples was in three steps. In two endothermic processes, water and ammonia are liberated. The third exothermic process corresponds to the decomposition of CN groups [Fig. 2(a) and (b)]. The main concern of this work was the study of the endothermic processes. It is very difficult to determine the sequence for the liberation of H_2O and NH_3, and also determination of whether a simultaneous liberation of both prod-

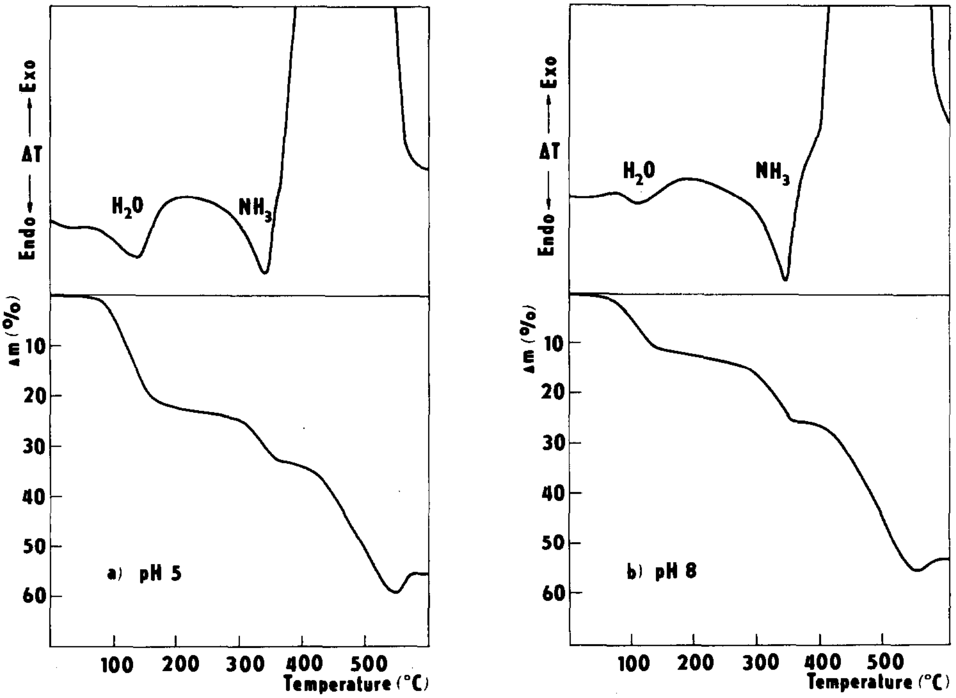

Fig. 2. TG and DTA curves of $Ni(NH_3)_mNi(CN)_4 \cdot n\ H_2O$. (a) pH 5: $m = 2$, $n = 4$, (b) pH 8: $m = 2$, $n = 1.9$.

ucts takes place, because their molecular weights are very close. DSC measurements were applied in order to achieve precise control of the atmosphere. In the case of the sample prepared at pH 8 the combination of DSC and GC was introduced.

DSC measurements (Fig. 3) on the sample of clathrate at 650 K show distinct peaks at 340 K and 550 K. These agree with the results of the TG and DTA analyses connected with the liberation of H_2O and NH_3. According to the DSC measurements alone it is not possible to state definitely the sequence for the liberation of gaseous products. Therefore for indication of water and ammonia loss in individual endothermic processes, a combination of DSC and GC methods was used.

The technique of DTA and GC and similar combinations have been described by Garn [18] and others [19]. The DSC/GC combination is not commonly used, in spite of the fact that the use of the differential calorimeter makes it possible. The application of DSC/GC analyses does not seem to be advantageous, because the carrier gas does not diffuse through the sample. This means that the decomposition of the compounds under study proceeds in an atmosphere of liberated gaseous product, which may influence its course and differ from the results of other thermoanalytical techniques.

According to our measurements on the clathrate compound samples, combination of the DSC/GC method enables the determination of individual components of the decomposition products (H_2O and NH_3, respectively). This combination will be more advantageous in the case of the simultaneous differentiation of more gaseous products. It is necessary to be selective when using materials for separation and to optimize the separation conditions in order to achieve a GC analysis in a short time.

On the basis of the different retention times found at 60°C [$t_R = 15$ min

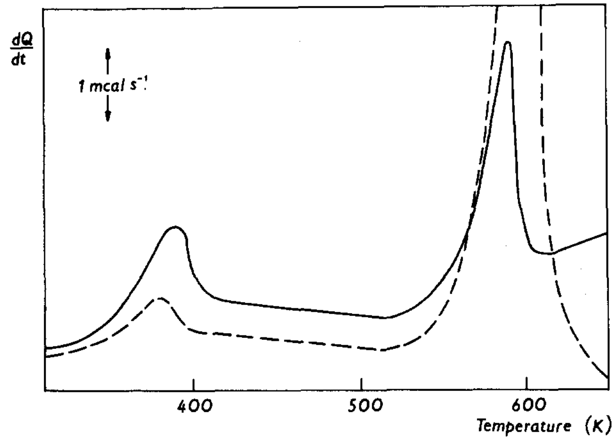

Fig. 3. DSC curves of $Ni(NH_3)_mNi(CN)_4 \cdot nH_2O$ clathrates prepared at pH 5 (————) and 8 (- - - - -).

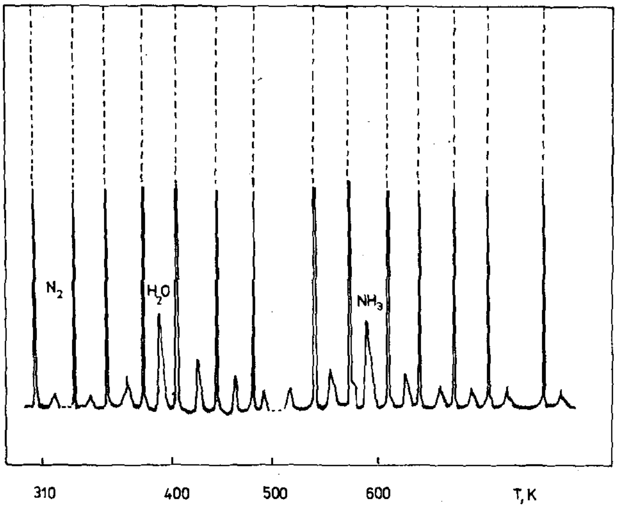

Fig. 4. Record of GC analyses of the decomposition products of $Ni(NH_3)_mNi(CN)_4 \cdot nH_2O$ studies by DSC.

(NH_3) and $t_R = 20$ min $(H_2O)]$, water is lost in the first step and ammonia in the second step (Fig. 4). The fact that the second peak in DSC measurements belongs to NH_3 was also tested with Nessler reagent. The vapors of the second liberated component were introduced directly into this reagent from the outlet of the DSC equipment. In the case of the first liberated component (H_2O) this test was negative.

The percentage content of H_2O and NH_3 and their mole composition in clathrate samples are summarized in Table 1. They are calculated from TG curves and compared with the results of the elemental analyses.

These results show that the change of the pH value of the solution has also changed the amount of sorbed water. The amount of water in the clathrate is increased in more acidic solution and decreased in more basic solution. It is necessary to note that the same pH value during the isolation of the compounds and the same conditions of preparation (the rate of mixing and cooling during the lowering of the pH of the solution by addition of acetic acid) should be kept in order to achieve the same quantity of bonded water.

TABLE 1

Content of water and ammonia in clathrate compounds prepared at different pH

$Ni(NH_3)_mNi(CN)_4 \cdot n\,H_2O$			NH_3(wt.%)		H_2O(wt.%)	
pH	*m*	*n*	calc.	found(TG)	calc.	found(TG)
8	2	1.9	11.75	12.5	11.81	11.8
7	2	2.0	11.68	12.0	12.35	12.8
6	2	2.5	11.32	11.8	14.98	15.0
5	2	4.0	10.39	10.5	21.99	22.0

The quantity of water *n* in the tetracyano complex and also the number of nitrogen-containing bases *m* present is influenced by the pH change. The water is enclosed between the layers, but it may also be present as a ligand in the first coordination sphere, or simultaneously in both forms if $n > 2$. The number of NH_3 ligands *m* present in the clathrate compounds prepared in solutions of pH 8–5 is 2.

These results show the importance of pH values of solutions during the synthesis of clathrate compounds $M(NH_3)_mM'(CN)_4 \cdot n$ G and equally $M(en)_mM'(CN)_4 \cdot n$ G. The host model compounds of these clathrates has a site for the guest component (G) during their preparation if they are in contact with G (G also being water). The number of ligands in excess is partially decomposed by lowering the pH value. In this way, the site is capable of accepting organic molecules and water molecules, respectively. The content of water changes with the change in pH of the solutions in the range pH 8–5.

The application of thermal analysis methods and especially the combination of differential scanning calorimetry and gas chromatography is very useful for better characterization of the thermal decomposition processes. The DSC/GC combination allows the separation and identification of individual parts of the host molecules.

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